Operando X-ray absorption and emission spectroscopic study of V-W-TiO₂ catalysts for NOx removal from the diesel exhaust

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A large number of heavy-duty diesel engines worldwide are equipped with vanadia-based catalysts for Selective Catalytic Reduction of NOx with NH₃ (NH₃-SCR). X-ray absorption spectroscopy (XAS) is a technique of choice for understanding changes in the oxidation state and coordination environment of active sites during real catalyst operation, i.e. operando [1]. V K edge X-ray absorption near edge structure (XANES) region is very sensitive to its oxidation state and coordination environment which makes it attractive also for catalysis research. However, so far in situ or operando studies on the realistic V-W/TiO₂ system have not been reported. The reason is a combination of highly absorbing W-containing support nearly prohibiting transmission XAS and abundant Ti Kβ₁,₂ lines of which overlap with V Kα₁,₂ , thus, prohibiting conventional fluorescence measurements. Using X-ray emission spectrometers based on crystal analyzers allows resolving Ti and V fluorescence lines and record high energy resolution fluorescence detected (HERFD)-XAS data on the realistic V-W/TiO₂ under working conditions.

A series of V-W/TiO₂ and V/TiO₂ catalysts with highly dispersed isolated and polymeric V oxo-species and high activity towards NH₃-SCR were synthesized by incipient wetness impregnation and grafting [2]. HERFD-XANES and XES measurements were carried out at ID26 beamline of the European Synchrotron Radiation Facility using a Johann-type emission spectrometer equipped with four spherically bent Ge (422) analyzer crystals. For collecting operando spectra a setup with a heated quartz capillary microreactor (plug flow geometry, diameter 1 mm, wall thickness 0.01 mm, heated with an air blower) was used, typical conditions were 1000 ppm NO or 1000 ppm NO₂, 1000 ppm NH₃, 5% O₂, 0-1.5% H₂O in He at 250 or 400 °C. Outlet gas analysis was performed using an MKS MultiGas 2030 FTIR.

Variations in the Kβ₁,₂ XES and the pre-edge region of HERFD-XANES indicate redox switching of V sites between V⁴⁺ and V⁵⁺ states during NH₃-SCR and under related model conditions. In contrast, the shape of V-K XANES spectra is very sensitive to variations in the coordination geometry, however, no significant changes in the HERFD-XANES were observed revealing an almost unchanged geometry of V sites u. The formation of a direct V-N bond was not observed in the valence-to-core region of the X-ray emission spectra compared to our earlier results in Cu- and Fe-based zeolites [3]. However, the slight changes of the vtc-XES region observed at low but also high temperatures, particularly in the presence of pure NH₃ and of NO+O₂, clearly suggest the adsorption of these species most probably via a neighboring O atom or at interfacial sites with the TiO₂ or WO₃/TiO₂ support.

The obtained information indicates that the role of V species in NH₃-SCR is to provide redox sites and also to facilitate the interaction between NH₃ and NO. The results of this first operando XAS/XES study of V-W/TiO₂ catalysts allow better understanding the SCR mechanism which may lead to improved catalyst design and better kinetic models.

References: